



Microwave-assisted molten-salt rapid synthesis of isotype triazine-/heptazine based g-C₃N₄ heterojunctions with highly enhanced photocatalytic hydrogen evolution performance

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ABSTRACT

Rapid synthesis and construction of graphitic carbon nitride (g-C₃N₄) based heterojunctions, cost-effective metal-free photocatalysts for hydrogen evolution reaction (HER) under solar irradiation, is of highly practical significance. This work reports a one-pot microwave-assisted molten-salt (mw-ms) process to rapidly synthesize isotype triazine-/heptazine based g-C₃N₄ heterojunctions with highly enhanced photocatalytic HER performance using melamine as the single-source precursor. The typical sample (mw-ms-g-C₃N₄) was obtained by thermally polymerizing melamine molecules at 550 °C for 30 min in the media of eutectic KCl/LiCl salts under microwave irradiation in air. The analyses of phases, chemical compositions and microstructures indicate that the mw-ms-g-C₃N₄ sample consists of an isotype triazine-/heptazine based g-C₃N₄ heterojunction, taking on a plate-like morphology with a specific surface area (*S*_{BET}) of 25.7 m² g^{−1}. Comparatively, the g-C₃N₄ sample synthesized via an electric-resistance molten-salt (er-ms) process at 550 °C for 240 min is composed of a triazine-based g-C₃N₄ phase with a *S*_{BET} of 58.1 m² g^{−1}, whereas the samples obtained by electric-resistance heating (er, at 550 °C for 240 min) and microwave heating (mw, at 550 °C for 30 min) processes consist of a heptazine-based g-C₃N₄ phase. The mw-ms-g-C₃N₄ sample shows a photocatalytic HER rate of 1480 μmol g^{−1} h^{−1}, which is 5 times that (300 μmol g^{−1} h^{−1}) of the er-ms-g-C₃N₄ sample, 15 times that (95 μmol g^{−1} h^{−1}) of the er-g-C₃N₄ sample and 23 times that (63 μmol g^{−1} h^{−1}) of the mw-g-C₃N₄ sample, under the similar visible-light (λ ≥ 420 nm) irradiation. The typical apparent quantum yield of the mw-ms-g-C₃N₄ sample at 420 nm is up to 10.7%. The UV–vis DR spectra suggest that both the triazine-based g-C₃N₄ and heptazine-based g-C₃N₄ phases have a similar bandgap of ~2.66 eV, whereas the Mott-Schottky analysis indicates that the triazine-based g-C₃N₄ phase has a more positive flat conductive potential (−0.90 V) than the triazine-based g-C₃N₄ phase (−1.22 V). Due to the suitable alignment of their energy bandgap structures, the isotype triazine-/heptazine based g-C₃N₄ hybrids in the mw-ms-g-C₃N₄ sample form a type II heterojunction of semiconductor/semiconductor, which provides a convenient carrier transfer path and leads to more efficient separation of photo-generated electron-hole pairs than the other samples. The synergistic effects of microwave heating and molten-salt liquid polycondensation provide a robust platform for rapid and large-scale construction of isotype g-C₃N₄/g-C₃N₄ heterojunctions as metal-free high-performance HER photocatalysts using a simple single-source precursor.

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1. Introduction

Hydrogen is a kind of clean energy, and photocatalytic water splitting for hydrogen evolution is a promising strategy to relieve increasing concern over the depletion of fossil fuels which are tightly associated with energy issues and pollution problems [1]. Though tremendous photocatalysts have been developed as water-

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splitting photocatalysts [2], some problems, such as complicated synthetic process, high cost and low utilization of solar light, still hinder the commercial applications of these photocatalysts [3,4]. To date, to develop novel photocatalysts with excellent and stable performance is still a challengeable task.

Recently, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a polymeric visible-light photocatalyst, has drawn increasing attention because of its suitable electric band-gap and efficient photocatalytic hydrogen evolution reaction (HER) activity [5,6]. Basically, the framework of $g\text{-C}_3\text{N}_4$ is composed of two basic tectonic units: one is the s-triazine ring and the other is the tri-s-triazine (or heptazine) ring which consists of three s-triazine rings connected by central N atoms [6,7]. As a typical metal-free photocatalyst, graphitic carbon nitride is beneficial from many aspects, e.g., plenty and low-cost precursors [8], excellent optical properties [9], and easy preparation [10]. However, for the $g\text{-C}_3\text{N}_4$ photocatalysts, the low separation efficiency of photogenerated electron-hole carries and their poor transfer ability are still obstacles for their practical applications. Also, the conventional thermal polycondensation of C, N-containing precursors is a time-consuming and low cost-effective process.

To further improve the performance of $g\text{-C}_3\text{N}_4$ photocatalysts, many scientists have developed multifarious strategies based on different principles, e.g., adjusting microstructures [11–14], forming defects [15–17], doping [18–20], forming heterojunctions [21–25], and adding carbon species [26–28]. These modification strategies mainly focus on shortening the distance of transfer paths, forming unique transmission channels or supporting more active sites for trapping carriers, and facilitating the separation and transmission of photogenerated electron-hole pairs. Band-alignment design for $g\text{-C}_3\text{N}_4$ photocatalysts, usually obtained by the traditional thermal polycondensation method, is an effective approach to enhance the separation and transmission of photogenerated carriers by forming nano-junctions at the interfaces. Compared to the heterojunctions constructed with the second-phase metals or semiconductors, the ones with isotype $g\text{-C}_3\text{N}_4$ phases are more fascinating. Wang et al. have reported a CNS-CN isotype heterojunction via a two-step thermal treating process, and the resultant sample was of excellent photocatalytic watersplitting performance [29]. Besides, the $g\text{-C}_3\text{N}_4$ isotype heterostructure has also been prepared by thermal polymerization of the mixed precursor of urea and thiourea [25]. However, there is still a big challenge to synthesize $g\text{-C}_3\text{N}_4$ isotype heterojunctions for HER photocatalysts from a single-source precursor (i.e., melamine) via a simple process.

Recently, some new strategies have been devolved to synthesize $g\text{-C}_3\text{N}_4$ based photocatalysts. For example, molten salts, unique high-temperature ionic liquids, have been used as the media to prepare polymeric carbon nitrides [30]. Schwinghammer et al. [31] have developed an electric-resistance heating molten-salt method to synthesize poly(triazine imide) (PTI) photocatalysts (i.e., triazine-based $g\text{-C}_3\text{N}_4$) with enhanced H_2 evolution performance. The above triazine-based $g\text{-C}_3\text{N}_4$ is an isotype of the heptazine-based $g\text{-C}_3\text{N}_4$ obtained by conventional electric-resistance thermal methods. Taking advantage of the molten-salt method, researchers can use templates [32], various precursors [33] and secondary semiconductors [34] to construct novel carbon nitride based photocatalysts. Besides $g\text{-C}_3\text{N}_4$, the molten-salt method has also been used to prepare other functional materials, e.g., graphitic carbon [35] and graphene [36]. The molten-salt process offers a unique liquid condition that is stable and convenient for high-temperature synthesis [37]. Though the electric-resistance heating molten-salt method can be used to synthesize high-performance graphitic carbon nitride photocatalysts, the problems of time consuming in synthesis and low efficiency in performance are still difficult to overcome.

Microwave irradiation, known as an efficient heating manner, benefits from its ultrafast heating rate due to dipolar polariza-

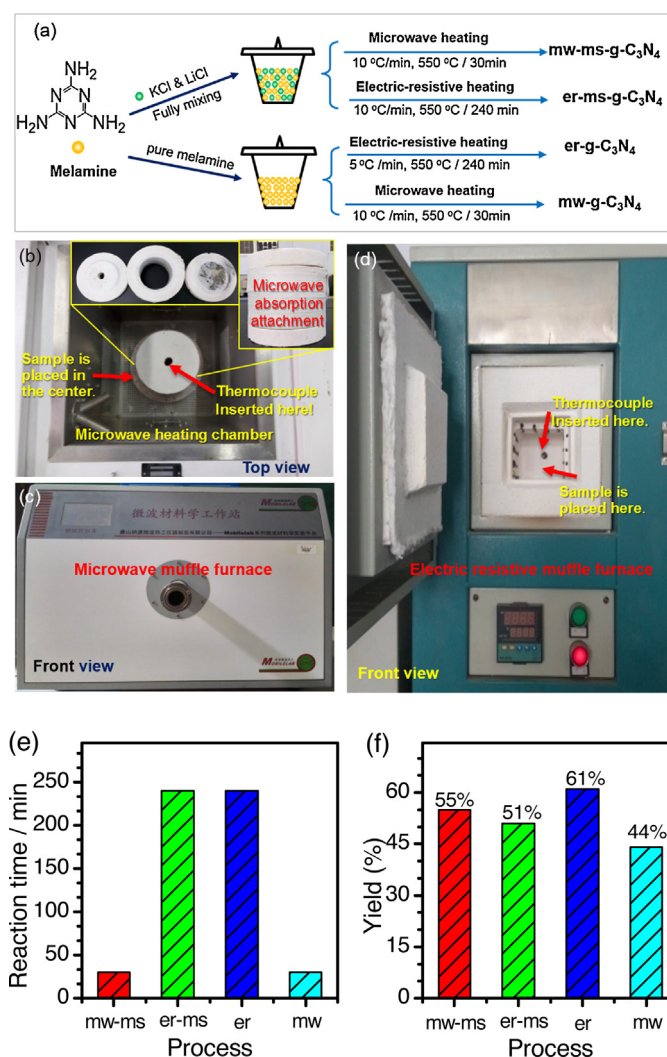


Fig. 1. Schematic illustration of the synthetic processes for graphitic carbon nitride photocatalysts from melamine: (a) Typical 4 thermal polymerization processes (mw-ms = microwave-assisted molten-salt process, er-ms = electric-resistance molten-salt process, er = electric-resistance heating, and mw = microwave-heating process); (b–c) Structure of the microwave workstation used; (d) Structure of the electric-resistance furnace used; (e) Comparison of polymerization times for various processes; (f) Comparison of typical yields of graphitic carbon nitride photocatalysts via the different processes.

tion or ionic conduction [38]. Yuan et al. [39] have reported a microwave-assisted heating method to synthesize a highly crystalline $g\text{-C}_3\text{N}_4$ photocatalyst in a few minutes, suggesting that the microwave heating is a potential way in rapid synthesis of carbon nitride based materials. To achieve a stable and reliable condition in a solid-state reaction system, many measures have to be considered under microwave irradiation, whereas the liquid reaction condition can provide a more stable microwave heating process [40]. Therefore, multifarious liquid phases, e.g., aqueous solutions [41], polyols [42] and ionic liquids [43], have been used as reaction media in the microwave-assisted processes to improve the stability of microwave heating.

We herein develop a microwave-assisted molten-salt (mw-ms) process to synthesize an isotype heterojunction of triazine/heptazine based $g\text{-C}_3\text{N}_4$ photocatalysts using easily available melamine as the single-source precursor. This process combines the advantages of rapid heating of microwave irradiation and high-temperature liquid media of molten-salt KCl/LiCl mixtures (Fig. 1a). By using this one-pot thermal polycondensation process,

a large-scale and rapid synthesis of high-quality HER photocatalysts of graphitic carbon nitride with a high yield of 55 wt.% has been achieved at 550 °C for 30 min, and the photocatalysts consist of unique isotype heterojunctions of triazine-/heptazine based g-C₃N₄ nanocrystals. For purposes of comparison, the conventional thermal polymerization methods, including electric-resistance heating (er), microwave heating (mw), and electric-resistance molten-salt (er-ms) process, are also used to synthesize g-C₃N₄ based photocatalysts (Fig. 1a). The photocatalytic HER activity of the isotype triazine-/heptazine based g-C₃N₄ heterojunctions is much higher than that of the g-C₃N₄ samples obtained by the above conventional thermal polymerization processes. The phases, chemical compositions, microstructures, optical properties and photocatalytic HER performance of the as-obtained samples are comparatively investigated, and the related mechanisms are analyzed.

2. Experimental section

2.1. Materials and setup

Melamine (chemically pure, Sinopharm Chemical Reagent Co. Ltd.), LiCl (analytically pure, Sigma-Aldrich), KCl (analytical pure, Tianjin Kermel Chemical Reagent Co. Ltd), triethanolamine (TEOA, analytically pure, Tianjin Fengchuan Chemical Reagent Co., Ltd), H₂PtCl₄·6H₂O (Shanghai Chemical Reagent Co., Ltd), and rhodamine B (RhB, analytically pure, Tianjin Kaitong Chemical Reagent Co., Ltd) were used as received. A commercially available microwave workstation (Mobilelab, Tangshan Nanosource Microwave Thermal Instrument Manufacturing Co. Ltd, Fig. 1b–c), and a conventional electric-resistance furnace (Fig. 1d, heating chamber dimensions: 100 × 100 × 120 mm) were used in the synthesis of g-C₃N₄ samples.

2.2. Materials synthesis

As Fig. 1 shows, four processes were comparatively used to synthesize g-C₃N₄ photocatalysts.

- (1) *Microwave-assisted molten-salt process (mw-ms-g-C₃N₄)*. The eutectic mixture of KCl/LiCl (49.4:50.6 in molar ratio) with a melting point about 450 °C was used as the molten salt. Typically, 1.26 g of melamine and 3 g of the above eutectic mixture of KCl/LiCl were fully mixed by grinding them in an agate mortar for more than 5 min. The as-obtained mixture containing melamine (~30 wt.%) and the eutectic salt (70 wt.%) was transferred into a ceramic crucible (20 mL in volume) with a ceramic lid. The above crucible was placed in the center of the microwave heating chamber (Fig. 1b), and then heated to 550 °C with a heating rate of 10 °C min^{−1}. The heating treatment was kept at 550 °C for 30 min, and then the sample was naturally cooled down to room temperature. The solid obtained was ground to micro-powders and washed with hot water (200 mL at ~80 °C, stirring for 1 h) to remove KCl/LiCl species. After filtration and washing for 4 times, the solid obtained was dried at 80 °C for more than 12 h. The as-obtained sample was marked as mw-ms-g-C₃N₄. For the sake of comparison, some g-C₃N₄ samples were also synthesized using eutectic KCl/LiCl mixtures with various melting points, e.g., 353 °C (KCl/LiCl = 40.8:59.2) and 400 °C (KCl/LiCl = 45:55), as the polymerization reaction media of melamine via the similar microwave-assisted molten-salt process, and the corresponding samples obtained were marked as mw-ms-353 °C-g-C₃N₄ and mw-ms-400 °C-g-C₃N₄, respectively. Effects of the factors influencing the polymerization reaction, e.g., reaction temperatures (520 °C, 550 °C, 580 °C)

and reaction times (15 min, 30 min, 45 min), were investigated using the eutectic KCl/LiCl mixture with a melting point of 450 °C as the reaction media.

- (2) *Electric-resistance molten-salt process (er-ms-g-C₃N₄)*. Typically, 1 g of melamine and 5 g of eutectic mixture of KCl/LiCl (40.8:59.2 in molar ratio) with a melting point of ~353 °C were fully ground in an agate mortar, and the as-obtained powder was then transferred to a ceramic crucible (20 mL), which was placed into the center of heating chamber of a muffle furnace (Fig. 1d). The furnace was heated to 550 °C with a heating rate of 10 °C min^{−1} and kept at 550 °C for 4 h. The as-obtained solid was ground and washed with hot water, and dried at 80 °C for more than 12 h, and the as-obtained sample was marked as er-ms-g-C₃N₄ [44].
- (3) *Electric-resistance heating process (er-g-C₃N₄)*. Typically, 10 g of melamine was put in a porcelain crucible (20 mL) covered with a lid, which was placed into the electric-resistance muffle furnace (Fig. 1d). The furnace was heated to 550 °C with heating rate of 5 °C min^{−1} and the polymerization reaction was kept at 550 °C for 4 h. The as-obtained sample was marked as er-g-C₃N₄.
- (4) *Microwave heating process (mw-g-C₃N₄)*. Typically, 10 g of melamine was put in a ceramic crucible (20 mL) covered with a lid. The crucible with melamine was placed into the center of the microwave heating chamber (Fig. 1b) and heated at 550 °C for 30 min with a heating rate of 10 °C min^{−1}. The as-obtained was marked as mw-g-C₃N₄.

2.3. Characterization and analysis

Phase compositions of the graphitic carbon nitrides obtained were determined by X-ray diffraction on a D/max 2500 XRD diffractometer (Rigaku) with a Cu Kα radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 30 mA, with a scanning rate of 4° min^{−1} in $2\theta = 10\text{--}60^\circ$. Fourier transform infrared spectra (FT-IR) were recorded on a FT-IR spectrometer (Thermo Fisher Nicolet i50) in the range of 4000–500 cm^{−1} at a resolution of 4 cm^{−1} using the KBr technique. Raman spectra were obtained using a Raman spectrometer (LabRAM HR Evolution, HORIBA JobinYvon, France) at room temperature using the 633 nm line as the excitation source. The powder samples were fixed on the surface of a SiO₂/Si substrate. The morphology was observed by scanning electron microscopy (JSM-7001F JEOL, Japan) and transmission electron microscopy (Tecnai F-20-S-TWIN, FEI, America). The UV–vis diffuse reflectance (DR) spectra were conducted on a UV–vis-NIR spectrophotometer (Shimadzu UV-3600) in a wavelength range of 200–800 nm. The photoluminescence (PL) spectra were identified on a spectrofluorometer (FluoroMax-4, HORIBA JobinYvon, France) at a 388 nm line laser at room temperature; the emission spectra (λ_{em}) ranged in 400–700 nm (with a 400 nm filter) and both of slits were 2 nm. The time-resolved transient PL (TR-PL) spectra were determined by using a spectrofluorometer (Fluorolog@-3 TCSPC, HORIBA, France) excited by 370 nm laser with emission at 460 nm. X-ray photoelectron spectroscopy (XPS) spectra were performed on an XPS spectroscope (Escalab 250xi, Thermo Scientific Ltd., England) equipped with an Al Kα (1486.6 eV) radiation source. The specific surface areas were measured by Brunauer-Enmet-Teller (BET) method on the basis of N₂ adsorption-desorption isotherms obtained on ASAP 2460 (Micromeritics) machine at a liquid nitrogen temperature (−196 °C). Elemental analysis of CHN was measured by a CHNS/O analyzer (Flash EA 112 series Thermo Scientific).

2.4. Photoelectrochemical test

The working electrodes (i.e., photoanodes) were prepared as follows: 5 mg of the g-C₃N₄ sample was dispersed in 250 μ L of dimethyl formamide (DMF) by ultrasonication for 30 min to make a uniform g-C₃N₄ slurry, which was then coated onto the surface of an FTO glass plate (2.5 \times 2.4 cm). Before use, the FTO glass plate was carefully washed with water, ethanol and acetone for 30 min sequentially, and the g-C₃N₄/FTO electrodes were dried in air for one day. Photoelectrochemical test was carried out in a standard three-electrode setup on an electrochemical workstation (AME-TEK, PARSTAT 4000, America). The electrodes of the Pt wire and Ag/AgCl (saturated KCl) were used as the counter and reference electrode, respectively. The Na₂SO₄ aqueous solution (0.2 M) was used as the electrolyte. A 300 W Xenon lamp (Beijing Perfectlight Co., Ltd) equipped with a cutoff filter ($\lambda \geq 420$ nm) was used as the light source. The photocurrent response spectroscopy was measured at a constant potential of +0.9 V vs. the working photoanode. The electrochemical impedance spectroscopy (EIS) was determined at an open-circuit voltage in a frequency range of 10 mHz–100 kHz with an amplitude of 5 mV. The Mott-Schottky plots were recorded on the electrochemical workstation (CHI660E Instruments) using a standard three-electrode system, with a working electrode of photoanodes, a reference electrode of Ag/AgCl and a counter electrode of Pt foil, in an electrolyte of 0.5 M Na₂SO₄ aqueous solution. The tests were carried on at a frequency of 1 kHz in a potential range of –1.5 to –1 V (vs. Ag/AgCl) under dark condition.

2.5. Test of photocatalytic hydrogen evolution

The test of photocatalytic hydrogen evolution reaction (HER) activity of the g-C₃N₄ samples was carried out in a commercially available HER system (CEL-SPH2N, Beijing China Education Au-light Co., Ltd., China). Typically, 50 mg of the g-C₃N₄ photocatalyst and 0.3 mL of H₂PtCl₄·6H₂O aqueous solution (0.0256 mol L^{–1}) were added in a Pyrex top-irradiation reaction vessel and then dispersed in 50 mL of triethanolamine aqueous solution (TEOA, 10 vol.%) by ultrasonication for 10 min. Then a co-catalyst of 3 wt% Pt was photo-deposited on the surfaces of the g-C₃N₄ samples by UV–vis irradiation (CEL-XHF 300, Beijing China Education Au-light Co., Ltd., China) for 1 h. The Pyrex reaction vessel with the g-C₃N₄ based photocatalyst was carefully fixed and sealed to the photocatalytic HER system, of which the air impermeability was carefully checked by being vacuumed and kept for more than 30 min. During the photocatalytic HER test, a 300 W Xenon lamp equipped with a 420 nm cut-off filter was used as the irradiation source. The amount of hydrogen generated was analyzed by a gas chromatographer (GC 7920, Beijing China Education Au-light Co., Ltd., China) using high-purity N₂ (99.999%) as the carrier gas.

The apparent quantum yield (AQY) of the g-C₃N₄ sample was measured by using a Xe lamp with a monochromatic light filter of 420 nm. The AQY was calculated as the follow equation (Eq. (1)) [60]:

$$AQY = \frac{N_e}{N_p} \times 100\% = \frac{2MN_Ahc}{SPt\lambda} \times 100\% \quad (1)$$

where, N_e and N_p mean the amounts of reaction electrons and incident photons, respectively; M is the amount of hydrogen molecules, and N_A , h and c are Avogadro's constant, Planck constant and the speed of light, respectively; S is the irradiation area, P is the intensity of irradiation, t means the photoreaction time, and λ is the wavelength of incident light ($\lambda = 420$ nm).

2.6. Test of photocatalytic degradation activity of rhodamine B

Photocatalytic degradation of rhodamine B (RhB) with the obtained g-C₃N₄ samples was conducted under a visible-light ($\lambda \geq 420$ nm) irradiation using a 300 W Xe lamp (NBET, HSX-F300) equipped with an ultraviolet cutoff filter (420 nm). The light density used was about 200 mW cm^{–2}. Typically, 50 mg of g-C₃N₄ sample was dispersed in a 50 mL aqueous solution of RhB (10 mg L^{–1}) (i.e., sonication for 5 min) under a dark condition by rigorously covering the above solution using an aluminum foil. Before visible-light irradiation, the above suspension was kept magnetically stirring in dark for 30 min to reach a dye-absorption equilibrium on the g-C₃N₄ photocatalysts. During the test of photocatalytic degradation, 5 mL of the suspensions were drawn from the reaction system every 10 min. The as-obtained suspensions drawn out were centrifuged at 5000 rpm for 5 min twice to remove the solid photocatalyst particles, and the upper clear solutions were then transferred to a quartz cuvette (1 \times 1 cm) to measure their absorption spectra using a UV–vis spectrophotometer (UV-1800PC, Mapada Instruments, China). According to the Lambert-Beer law ($A = \lg(1/T) = kC$), the RhB concentrations (C) of the solutions are in direct proportion to their absorbance (A) at 551 nm.

3. Results and discussion

3.1. Synthesis, photocatalytic and photoelectrochemical properties

The graphitic carbon nitride (g-C₃N₄) sample of mw-ms-g-C₃N₄ was firstly synthesized using the microwave-assisted molten-salt (mw-ms) process (Fig. 1) at 550 °C for 30 min with melamine as the single-source precursor. For the sake of comparisons, three typical g-C₃N₄ samples were synthesized by electric-resistance molten-salt process (er-ms-g-C₃N₄), electric-resistance heating process (er-g-C₃N₄) [8,44], and microwave heating process (mw-g-C₃N₄). Fig. 1e and f compare the reaction times and typical yields of g-C₃N₄ in the various synthetic processes. When compared with the er process (51–61%, 240 min) and the mw one (44%, 30 min), the mw-ms process gives a higher yield of 55% in a shorter reaction time of 30 min.

Firstly, the HER activity of the g-C₃N₄ samples was comparatively evaluated. Fig. 2a shows the typical curves of the amount of H₂ generated as a function of irradiation time in the presence of g-C₃N₄ samples loading ~3 wt.% Pt in 10 vol.% TEOA aqueous solution upon exposure to visible-light irradiation ($\lambda \geq 420$ nm). The hydrogen amounts generated increase linearly with the irradiation times for the four samples. After reaction for 4 h, the cumulative hydrogen amount of mw-ms-g-C₃N₄ is up to 304 μ mol, whereas the cumulative hydrogen amounts of the samples of er-ms-g-C₃N₄, er-g-C₃N₄, and mw-g-C₃N₄ are 60, 19 and 13 μ mol, respectively. Fig. 2b compares the HER rates of the g-C₃N₄ samples. The HER rate of mw-ms-g-C₃N₄ is about 1480 μ mol g^{–1} h^{–1}, which is 5 times that (300 μ mol g^{–1} h^{–1}) of er-ms-g-C₃N₄, and 15 times that (95 μ mol g^{–1} h^{–1}) of er-g-C₃N₄ and 23 times that (63 μ mol g^{–1} h^{–1}) of mw-g-C₃N₄. It is worth noting that the g-C₃N₄ sample obtained by the mw-ms process has the highest HER activity under the visible-light condition among the four samples. In addition, the apparent quantum yield (AQY) of the mw-ms-g-C₃N₄ sample was measured at an incident light wavelength of $\lambda = 420$, and its typical AQY is as high as 10.7%, which is competitive in the existing literature reports of g-C₃N₄ photocatalysts for HER applications [44,64–66].

The photocurrents and electrochemical impedance spectroscopies of the g-C₃N₄ samples obtained via various processes were investigated for furthermore understanding their photoelectric

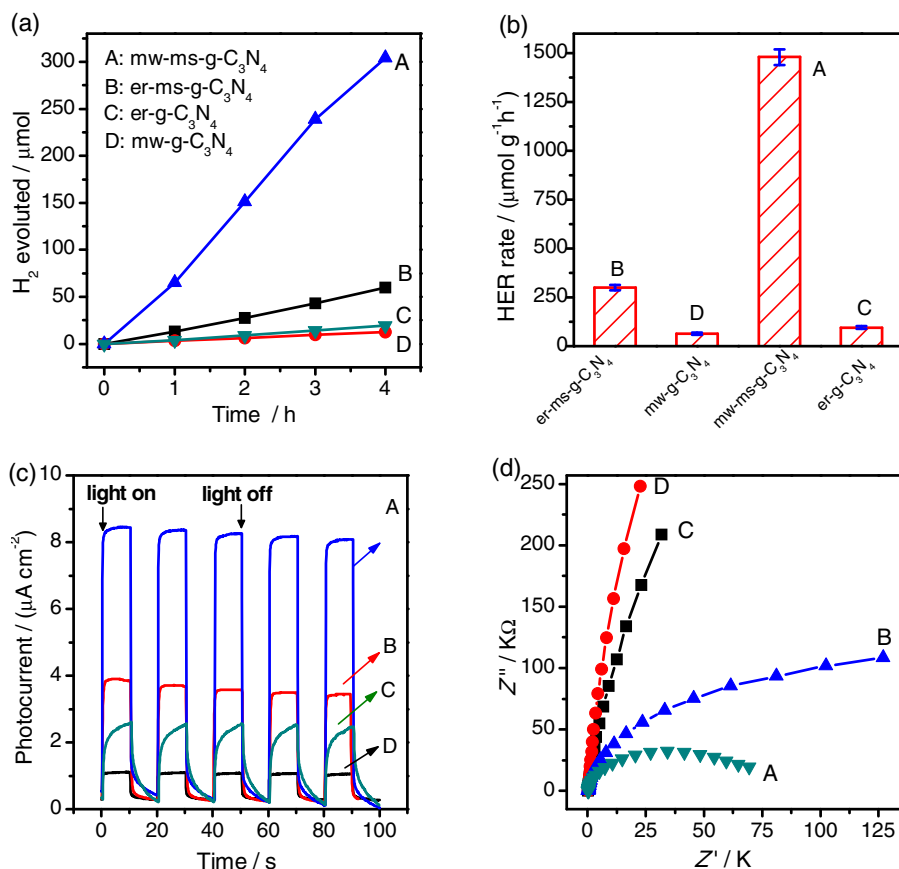


Fig. 2. (a) Amounts of photocatalytic hydrogen evolution as a function of reaction time under visible light irradiation ($\lambda \geq 420$ nm) in the presence of g-C₃N₄ samples obtained by different processes; (b) Comparison of the rates of photocatalytic H₂ evolution; (c) Transient photocurrents recorded under visible light irradiation ($\lambda \geq 420$ nm); (d) The EIS Nyquist plots of the 4 samples: (A) mw-ms-g-C₃N₄, (B) er-ms-g-C₃N₄, (C) er-g-C₃N₄, and (D) mw-g-C₃N₄.

performance. Fig. 2c shows the transient photocurrent vs. irradiation time recorded under visible light irradiation ($\lambda \geq 420$ nm). The mw-ms-g-C₃N₄ sample (A) shows a significantly enhanced photocurrent upon exposure to visible light irradiation compared with the other g-C₃N₄ samples (B–D). Also, the g-C₃N₄ samples (A and B) obtained by the molten-salt process show higher photocurrent responses than those (C and D) obtained direct thermo-polymerization. The transient photocurrent response is a qualitative approach to investigate the separation efficiency of photo-generated electron-hole pairs [45]. The highest photocurrent for the mw-ms-g-C₃N₄ sample indicates that this sample is of the highest efficiency in separation of photo-generated electron-hole pairs. Electrochemical impedance spectroscopy (EIS) is an intuitional approach to determine the electron transfer efficiency. Fig. 2d shows the EIS Nyquist plots of the g-C₃N₄ samples obtained. The arc radius of the semicircular Nyquist plot for the mw-ms-g-C₃N₄ sample (A) obtained by microwave-assisted molten-salt process is much smaller than that of the other g-C₃N₄ samples (B–D), suggesting that the mw-ms-g-C₃N₄ sample has the smallest electron-transfer resistance and the highest electrical conductivity. The EIS result highly agrees with the photocurrent response and photocatalytic HER performance of the g-C₃N₄ samples obtained via various processes.

3.2. Phase composition, morphology and microstructure

To understand their photocatalytic HER behavior, we carefully characterized the phase compositions, morphologies and microstructures of the g-C₃N₄ samples using the typical techniques of X-ray diffraction (XRD), elemental analysis (EA), Fourier trans-

form infrared (FT-IR) spectroscopy, SEM, N₂ adsorption-desorption isotherms, TEM and X-ray photoelectron spectroscopy (XPS).

The phases of the g-C₃N₄ samples were determined by the XRD analysis, and Fig. 3a shows their typical XRD patterns. The samples of mw-g-C₃N₄ (D) and er-g-C₃N₄ (C) show two diffraction peaks at $2\theta = 13.0^\circ$ and 27.4° . The strong peaks at 27.4° , due to the stacking of conjugated aromatic rings in the discotic systems, can be assignable to the (002) plane of the typical g-C₃N₄ phase (i.e., heptazine-based g-C₃N₄), and the weak one locates at $2\theta = 13.0^\circ$ can be recognized as the (100) plane, corresponding to the in-plane arrangement of nitrogen-linked heterocyclic rings [8]. The XRD pattern (B) of er-ms-g-C₃N₄ shows a series of peaks at 12.0° , 21° , 24.3° , 26.4° , 29.1° and 32.4° , which can be indexed to the deflections from the (100), (110), (200), (002), (102) and (210) planes of the poly(triazine imide) (PTI) phase (i.e., triazine-based g-C₃N₄), and the (100) and (002) diffraction planes correspond to the in-plane arrangement of nitrogen-linked heterocyclic rings and the stacking of the conjugated aromatic rings, respectively [31]. Comparatively, the XRD pattern of the mw-ms-g-C₃N₄ sample (A) seems to be a superimposition of pattern B and C. The peaks at 12.0° , 21° , 24.3° , 26.4° , 29.1° and 32.4° can be indexed to the triazine-based g-C₃N₄ phase, whereas the peak at $\sim 27.8^\circ$ can be indexed to the (002) plane of the heptazine-based g-C₃N₄ phase. When compared with er-g-C₃N₄ and mw-g-C₃N₄, the diffraction peak from the (002) plane of the mw-ms-g-C₃N₄ sample moves from 27.4° to 27.8° , which suggests that the mw-ms-g-C₃N₄ sample is of a decreased interlayer distance [46,47]. According to the XRD results, the samples of mw-g-C₃N₄ (D) and er-g-C₃N₄ (C) have a heptazine-based g-C₃N₄ phase, and the er-ms-g-C₃N₄ sample consists of a triazine-based g-C₃N₄

Table 1
Summary of elemental analysis, hydrogen evolution rate and yields of the g-C₃N₄ samples.

Sample	C (wt.%)	N (wt.%)	H (wt.%)	Apparent formula	Atomic C/N ratio	H ₂ rate (μmol g ⁻¹ h ⁻¹)	Reaction temperature and period	Yield (wt.%)
mw-ms-g-C ₃ N ₄	28.4	45.7	2.4	C _{3.0} N _{4.1} H _{3.0}	0.73	1480	550 °C/30 min	55
er-ms-g-C ₃ N ₄	24.4	40.2	2.3	C _{3.0} N _{4.2} H _{3.4}	0.71	300	550 °C/240 min	51
er-g-C ₃ N ₄	34.7	62.6	1.7	C _{3.0} N _{4.6} H _{1.7}	0.65	93	550 °C/240 min	61
mw-g-C ₃ N ₄	34.6	61.1	1.9	C _{3.0} N _{4.5} H _{2.0}	0.67	65	550 °C/30 min	44

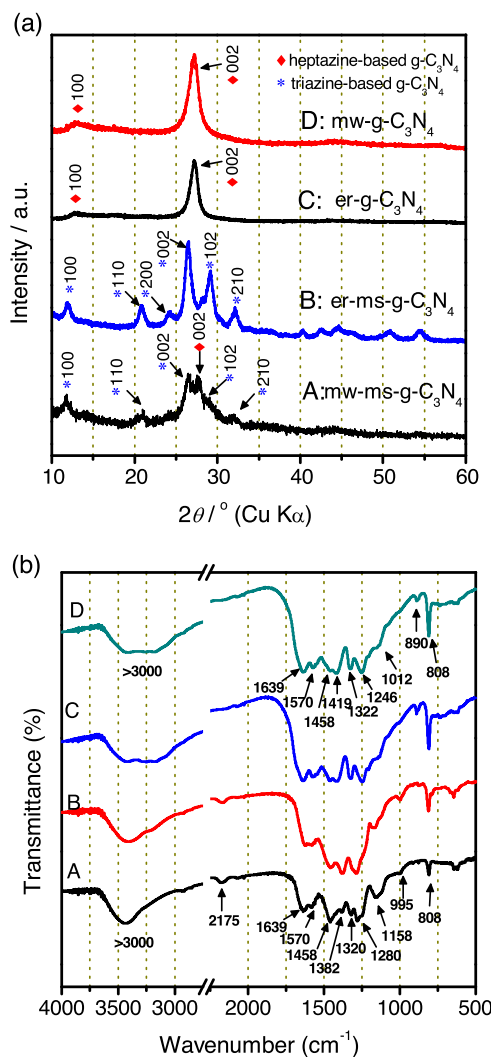


Fig. 3. (a) Typical XRD patterns (b) FT-IR spectra of the g-C₃N₄ photocatalysts obtained via different processes: (A) mw-ms-g-C₃N₄, (B) er-ms-g-C₃N₄, (C) er-g-C₃N₄, and (D) mw-g-C₃N₄.

phase; while the mw-ms-g-C₃N₄ sample is composed of the hybrid of triazine-based g-C₃N₄ and heptazine-based g-C₃N₄ phases.

The elemental analysis (EA) data (e.g., CHN results) of the as-obtained g-C₃N₄ samples are listed in Table 1. Calculated according to the CHN results, the apparent formula of mw-ms-g-C₃N₄, er-ms-g-C₃N₄, er-g-C₃N₄ and mw-g-C₃N₄ can be C_{3.0}N_{4.1}H_{3.0}, C_{3.0}N_{4.2}H_{3.4}, C_{3.0}N_{4.6}H_{1.7} and C_{3.0}N_{4.5}H_{2.0}, respectively. The EA results of er-g-C₃N₄ and mw-g-C₃N₄ are similar to the literature data [44]. The elemental compositions of mw-ms-g-C₃N₄ and er-ms-g-C₃N₄ are similar, but the atomic C/N ratio of mw-ms-g-C₃N₄ is slightly larger than that of er-ms-g-C₃N₄. This result suggests that the microwave-assisted molten-salt process favors in forming more N vacancies [48].

The chemical compositions of the g-C₃N₄ samples are further determined by FT-IR spectra, shown as Fig. 3b. One can see that the

FT-IR spectrum of mw-ms-g-C₃N₄ is similar to that of er-ms-g-C₃N₄ (spectra A, B in Fig. 3b), and that the FT-IR spectra of er-g-C₃N₄ and mw-g-C₃N₄ are similar (spectra C, D in Fig. 3b). The similarity in FT-IR spectra agrees with their XRD results (Fig. 3a). For the samples of er-g-C₃N₄ (C) and mw-g-C₃N₄ (D), the strong bands at 808 cm⁻¹ are assignable to the breathing mode of triazine-based units, and the peaks in the region of 1000–1700 cm⁻¹ can be attributed to the stretching mode of CN heterocycles [30]. The peaks at 1246, 1322 and 1419 cm⁻¹ correspond to the vibrations of aromatic N–C groups, and the peaks at 1570 and 1639 cm⁻¹ are due to the C=N vibrations. The bands in the region of >3000 cm⁻¹ can be assigned to secondary and primary amines and their intermolecular hydrogen bonding [30,48,49]. From the FT-IR spectrum (A) of mw-ms-g-C₃N₄, similar to that (B) of er-ms-g-C₃N₄, one can find that the intensity of the broad band at 3250 cm⁻¹ is weaker than that of the spectra C and D, suggesting that the amount of –NH groups in mw-ms-g-C₃N₄ and er-ms-g-C₃N₄ is less than that of er-g-C₃N₄ and mw-g-C₃N₄ [8]. The distinct bands at ~2175 cm⁻¹ in mw-ms-g-C₃N₄ and er-ms-g-C₃N₄ (A, B) indicate the presence of terminal cyano groups [33]. Some characteristic peaks in the FT-IR spectra, e.g., the peaks at 890 cm⁻¹ in er-g-C₃N₄ and mw-g-C₃N₄ and the peaks at 995, 2175 cm⁻¹ in mw-ms-g-C₃N₄ and er-ms-g-C₃N₄, can corroborate the difference in surface chemical compositions, although they are difficult to be indexed to any specific species. Raman spectra were also used to characterize these g-C₃N₄ samples (Fig. S2, ESI†), but no obvious peaks can be found in their Raman spectra.

The morphologies of the g-C₃N₄ samples were observed comparatively by SEM, and Fig. 4 shows their typical SEM images. According to the SEM images, all the samples seem to consist of large particulate bulks, which are composed of various sub-particles. For mw-ms-g-C₃N₄ (Fig. 4a), the bulks seem to be loose aggregates of nanoplates [50]. Comparatively, the er-ms-g-C₃N₄ sample (Fig. 4b) consists of rod-like particles, which are the assembly of smaller g-C₃N₄ nanorods (~100 nm in diameter); the samples of er-g-C₃N₄ (Fig. 4c) and mw-g-C₃N₄ (Fig. 4d) consist of large and compact g-C₃N₄ particles.

The specific surface areas and microstructures of the g-C₃N₄ samples obtained via different processes were characterized using N₂ adsorption-desorption isotherms. Fig. 5 shows their typical N₂ adsorption-desorption isotherms, which show a similar shape of type IV for all samples. The specific surface areas calculated by the BET method (*S*_{BET}) are 25.7, 58.1, 10.6, and 7.1 m² g⁻¹, for mw-ms-g-C₃N₄ (A), er-ms-g-C₃N₄ (B), er-g-C₃N₄ (C) and mw-g-C₃N₄ (D), respectively. Taking their SEM images (Fig. 4) into account, the samples of mw-ms-g-C₃N₄ and er-ms-g-C₃N₄ have larger *S*_{BET} values than those of er-g-C₃N₄ (C) and mw-g-C₃N₄ (D), indicating that molten-salt media are helpful to synthesize g-C₃N₄ with higher specific surface areas. It is worth noting that the HER activity of the mw-ms-g-C₃N₄ sample is much higher than that of the er-ms-g-C₃N₄ sample, although the *S*_{BET} of mw-ms-g-C₃N₄ is smaller than that of er-ms-g-C₃N₄. Therefore, the specific surface area is not the essential factor determining the photocatalytic performance of the g-C₃N₄ samples. Also, among the four g-C₃N₄ samples, mw-ms-g-C₃N₄ shows the best dispersibility in water (Fig. S3, ESI†). The higher dispersibility can achieve more uniformly, sufficient photo-deposition of Pt co-catalyst [51], and then be helpful to achieve a higher photocatalytic HER activity.

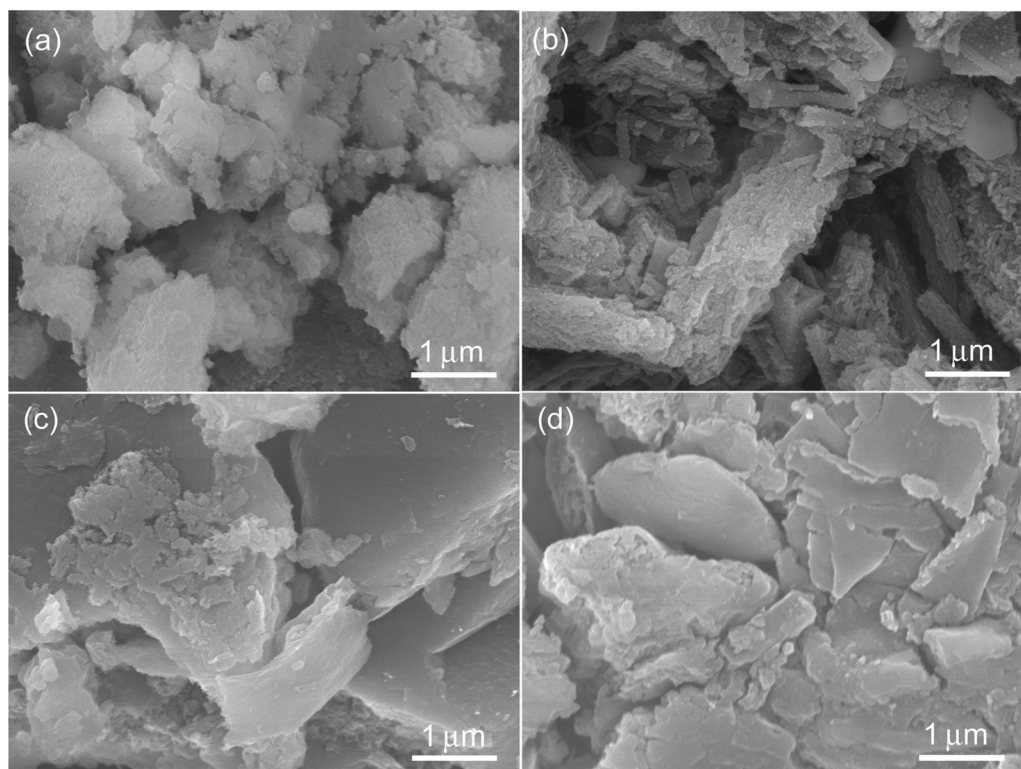


Fig. 4. Typical SEM images of the as-obtained g-C₃N₄ samples: (a) mw-ms-g-C₃N₄, (b) er-ms-g-C₃N₄, (c) er-g-C₃N₄, and (d) mw-g-C₃N₄.

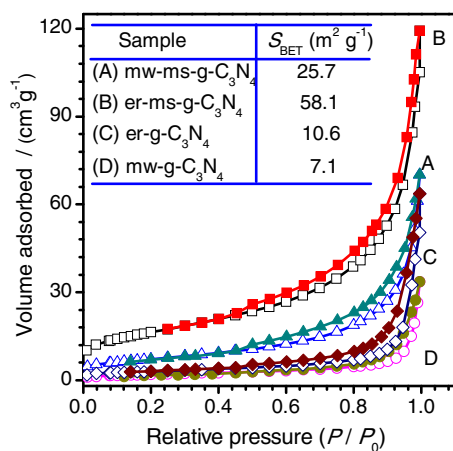


Fig. 5. Nitrogen adsorption-desorption isotherms of the as-obtained g-C₃N₄ samples: (A) mw-ms-g-C₃N₄, (B) er-ms-g-C₃N₄, (C) er-g-C₃N₄, and (D) mw-g-C₃N₄.

For further understanding the microstructures, we observed the typical g-C₃N₄ samples of mw-ms-g-C₃N₄ and er-ms-g-C₃N₄ using a TEM microscope (Fig. 6). Fig. 6a–e shows the TEM images of mw-ms-g-C₃N₄. The low-magnification TEM images (Fig. 6a, b) indicate that the mw-ms-g-C₃N₄ sample consists of thin plate-like particles. The enlarged TEM images (Fig. 6c, d) show that some small fragments are attached on the surfaces of the large plate-like particles. A high-resolution TEM (HR-TEM) image in Fig. 6e shows that most part of the large plate is amorphous, but some islands (e.g., point A) are well crystallized. The diffraction ring and some dots in the selected area electron diffraction (SAED) pattern (inset of Fig. 6e) corroborate the above HRTEM observations. As the HRTEM image of point A (inset of Fig. 6e) shows, the clear spacing of 0.336 nm can be indexed to the (002) facets of polymer triazine imide [30]. Comparatively, the TEM images of er-ms-g-C₃N₄ are shown in Fig. 6f–i. The

low-magnification TEM images (Fig. 6f, g) suggest that the er-ms-g-C₃N₄ sample consists of rod-like particles, which are aggregates of smaller g-C₃N₄ nanorods. The enlarged TEM image in Fig. 6h indicates that the small g-C₃N₄ nanorods with a diameter of ~25 nm are crystalline. As Fig. 6i shows, the loose aggregates of g-C₃N₄ nanorods form pores, resulting in a larger S_{BET} value.

The specific bonding and surface chemical states of the mw-ms-g-C₃N₄ sample was further characterized using XPS spectra and Fig. 7 shows its typical XPS spectra. The survey scan in Fig. 7a indicates that there are elements of C, N, O, K and Cl in the ms-mw-g-C₃N₄ sample. Clearly, elemental C and N belong to g-C₃N₄, O may be due to the O-containing species adsorbed, and elemental K and Cl should be the residue of molten salt (KCl) entrapped in the framework of the g-C₃N₄ structure. Fig. 7b shows the high-resolution XPS spectrum of C1s, of which there are three peaks at 284.8, 286.5 and 288.3 eV according to the peak fitting result. The peak at 288.3 eV corresponds to C=N=C in the heterocycle rings, the peak at 286.5 eV is due to C–OH, and the peak at 284.8 eV is assignable to C=C in adventitious carbon [8]. Besides, the peaks at 293.0 and 295.8 eV are assignable to K 2p of K⁺ [33]. Fig. 7d shows the O1s XPS spectrum, of which the peak at 532.0 eV indicates the existence of N–C–O groups and the one at 533 eV belongs to surface adsorbed water [52]. Fig. 7c shows the XPS spectrum of N1s, which can be subdivided to be four peaks at 398.8, 399.4, 400.7 and 404.2 eV, corresponding to sp²-hybridized nitrogen (C=N=C), tertiary nitrogen (NC₃), amino functional groups (NH_x groups) and π excitation, respectively [25]. The tertiary nitrogen peak at 399.4 eV confirms the presence of the heptazine heterocyclic structure [25]. According to the XPS spectra, the atomic ratio of NC₃ to C=N=C is 1:8.6, which is less than the theoretical value (1:6) of the pure heptazine ring. What's more, the atomic ratio of ring nitrogen (NC₃ and C=N=C) to amine nitrogen (NH_x) is 3.3:1, which is less than the theoretical value (7:2) of the heptazine ring but larger than 2:1 of the triazine ring. This result suggests that the mw-ms-g-C₃N₄ sample probably consists of the hybrid of heptazine ring and tri-

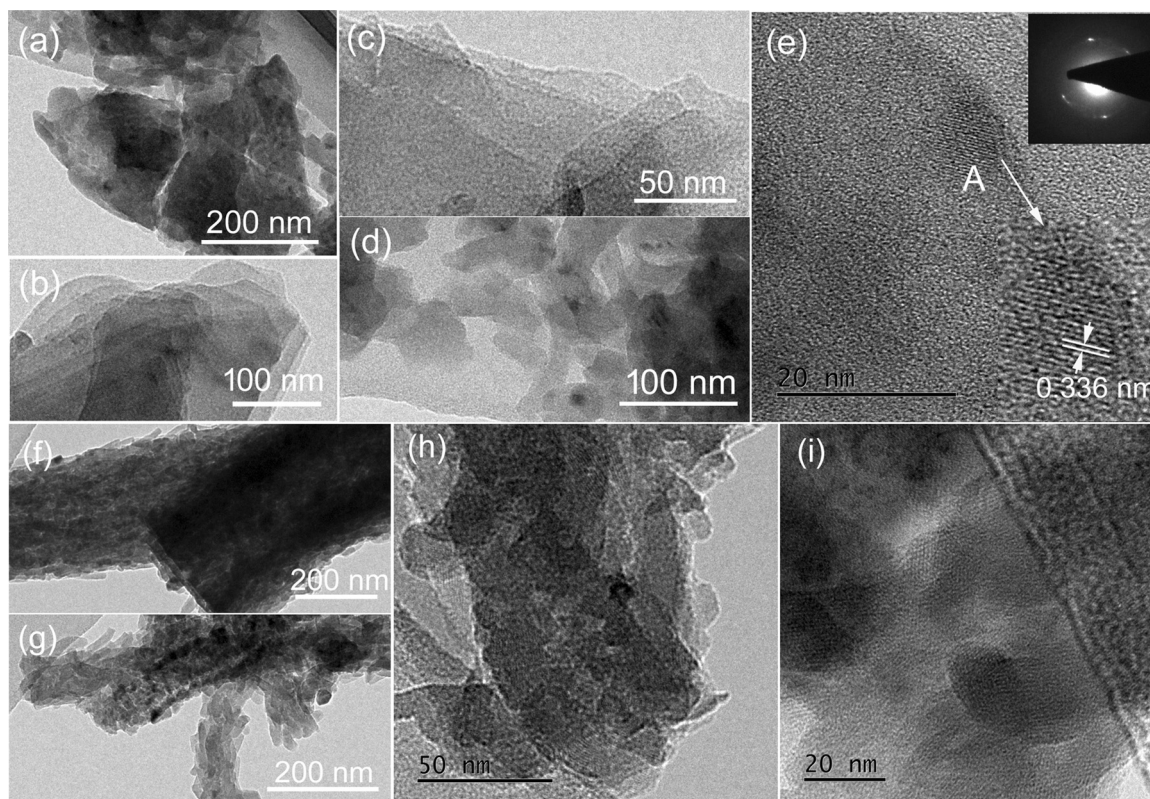


Fig. 6. Typical TEM images of the g-C₃N₄ samples obtained via (a–e) the microwave-assisted molten-salt process (mw-ms-g-C₃N₄), and (f–i) the electric-resistance molten-salt process (er-ms-g-C₃N₄).

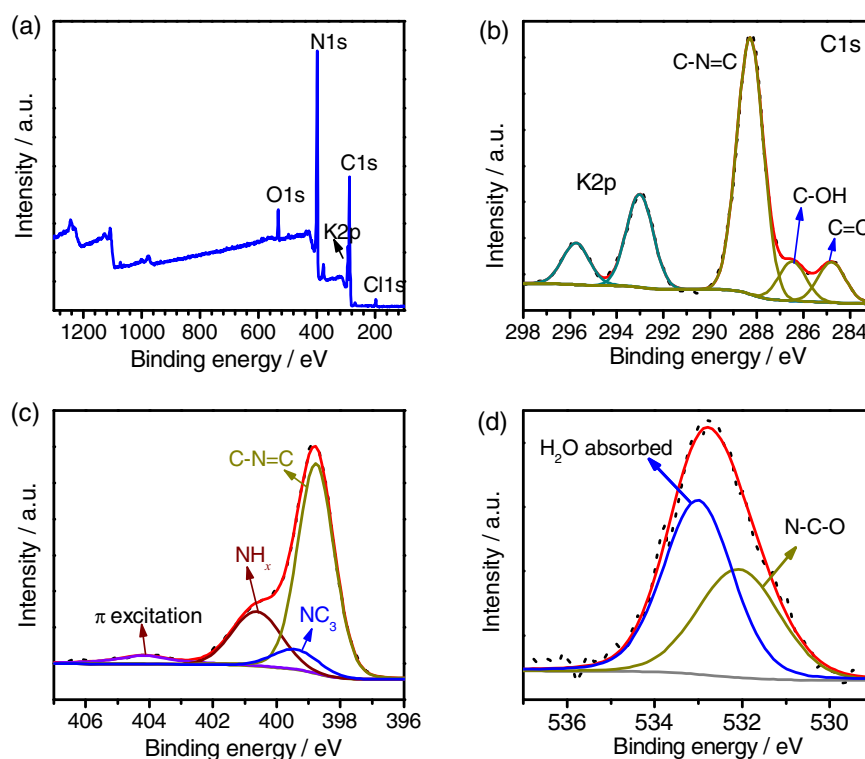


Fig. 7. XPS spectra of the g-C₃N₄ sample (mw-ms-g-C₃N₄) obtained via the microwave-assisted molten-salt process: (a) survey scan, (b) C1s, (c) N1s, and (d) O1s.

azine ring. According to the XPS results, the atomic ratio of C/N is 0.72, which is very close to 0.73 calculated by EA analysis in Table 1, suggesting the reliability of the composition analysis. According to

the above XPS analysis and their theoretic structures, the molar ratio of the triazine-based units and heptazine-based units in the mw-ms-g-C₃N₄ sample is about 13:15, close to 1:1.

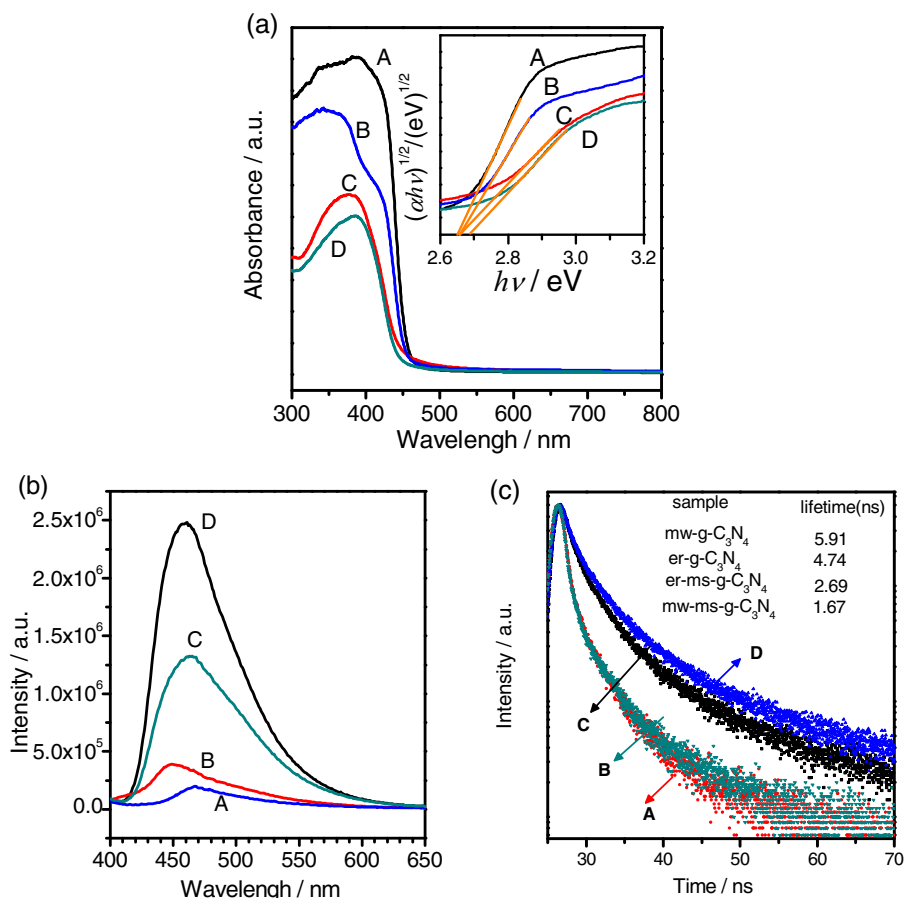


Fig. 8. (a) UV-vis absorption spectra converted from reflection to absorbance by the standard Kubelka–Munk method and the corresponding plots of $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$) for the band gap energy of as-obtained g-C₃N₄ samples; (b) Photoluminescence (PL) spectra of the g-C₃N₄ samples under 388 nm excitation at room temperature; (c) Time-resolved transient PL decay spectra of the g-C₃N₄ samples probed at 460 nm (excited by a 370 nm laser): (A) mw-ms-g-C₃N₄, (B) er-ms-g-C₃N₄, (C) er-g-C₃N₄, and (D) mw-g-C₃N₄.

Taking the XPS, EA and XRD results into account, we can conclude that the heptazine-based g-C₃N₄ and triazine-based g-C₃N₄ are co-existence in the sample of ms-mw-g-C₃N₄. The heptazine-based rings and triazine-based rings can be connected one another, and some K⁺ ions and other vacancies can be fixed in the rings or between them [53]. The possible formation mechanism will be discussed later. Therefore, the ms-mw-g-C₃N₄ sample consists of isotype triazine/heptazine based g-C₃N₄ heterojunctions, the er-ms-g-C₃N₄ sample consists of triazine-based g-C₃N₄ phase (PTI), and the samples of er-g-C₃N₄ and mw-g-C₃N₄ are composed of the heptazine based g-C₃N₄ phase. The difference in phases may account for their difference in photocatalytic HER performance.

3.3. Understanding of formation mechanism and enhancement in performance

For further understanding of the electronic band structures and photocatalytic properties, the UV-vis spectra, photoluminescence (PL) spectra and time-resolved transient PL decay (TR-PL) spectra were used to characterize the g-C₃N₄ samples obtained by various processes.

Fig. 8a shows the UV-vis absorption spectra converted from reflection to absorbance by the standard Kubelka–Munk method. The as-obtained g-C₃N₄ samples show obvious absorption from UV to ~460 nm, and the characteristic absorption at around 380 nm can be attributed to π - π^* electron transition in the conjugated aromatic ring system. In order to calculate the band gaps, the corresponding $(\alpha h\nu)^{1/2}$ was plotted versus the photon energy ($h\nu$) [51], and the

results are shown in the inset of Fig. 8a. According to the linear-fit lines, the band gaps of mw-ms-g-C₃N₄ (A), er-ms-g-C₃N₄ (B), er-g-C₃N₄ (C) and mw-g-C₃N₄ (D) are calculated to be $E_g(A) = 2.65$ eV, $E_g(B) = 2.66$ eV, $E_g(C) = 2.66$ eV and $E_g(D) = 2.70$ eV, respectively, by extrapolating their plots to $(\alpha h\nu)^{1/2} = 0$. Judging from their curve shapes, the UV-vis absorption spectrum (A) of mw-ms-g-C₃N₄ can be seen as a superimposition of the er-ms-g-C₃N₄ (B) and mw-g-C₃N₄ (D) samples.

The photoluminescence (PL) spectra of the g-C₃N₄ samples obtained are shown in Fig. 8b. We can see that the samples of er-g-C₃N₄ and mw-g-C₃N₄ show a strong intrinsic PL peak at ~464 nm, while the mw-ms-g-C₃N₄ sample presents the lowest intensity in PL spectra. The density of the PL emission spectra can be seen as a scale to measure the degree of recombination of photo-generated electron-hole pairs [45]. The lower the PL intensity indicates the less recombination of photo-generated electron-hole pairs, and the less recombination favors in enhancing the photocatalytic HER performance [15]. The PL results well account for the difference of the photocatalytic HER performance (Fig. 2) of the g-C₃N₄ samples.

For better understanding the transfer of the photogenerated charge carriers, we characterized the g-C₃N₄ samples using the time-resolved transient PL decay (TR-PL) spectra, excited by a 370 nm laser and probed at 460 nm, to probe the lifetime of the photo-excited charge carriers [61,62]. Typical TR-PL spectra of the 4 g-C₃N₄ samples (i.e., mw-ms-g-C₃N₄, er-ms-g-C₃N₄, er-g-C₃N₄ and mw-g-C₃N₄) are shown in Fig. 8c. Their corresponding radiative lifetimes with different percentages are shown in Table 2. Lifetime τ_1 is according to free excitons recombination, while τ_2 and τ_3 are

Table 2

Summary of the analyses of the time-resolved transient PL decay spectra of the g-C₃N₄ samples.

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_3 (ns)	A_3 (%)	τ (ns)
mw-ms-g-C ₃ N ₄	1.90	29.28	9.33	10.92	0.16	59.81	1.67
er-ms-g-C ₃ N ₄	2.82	26.87	0.67	64.29	17.94	8.35	2.68
er-g-C ₃ N ₄	3.28	50.7	0.73	27.27	13.04	22.03	4.74
mw-g-C ₃ N ₄	3.42	50.54	0.54	20.56	14.08	28.90	5.91

caused by non-radiative recombination which are attributed by de-trapping of charge carriers [63]. Their relaxation can be described by three time constants: τ_1 , τ_2 and τ_3 (Table 2). The weighted average recovery lifetimes are 1.67, 2.68, 4.74 and 5.91 ns for mw-ms-g-C₃N₄, er-ms-g-C₃N₄, er-g-C₃N₄ and mw-g-C₃N₄, respectively. It is well known that the average recovery lifetime can be regarded as a rational measure for evaluating the efficiency of photogenerated electron–hole separation involved in the investigated system [61,62]. The lifetime (1.67 ns) of mw-ms-g-C₃N₄ is shorter than those of the other samples (i.e., er-ms-g-C₃N₄, er-g-C₃N₄ and mw-g-C₃N₄). When considering the photocatalytic HER performance (Table 1), one can find that the shorter the lifetime, the larger the H₂ photo-generation rate. This trend can be understood that a decreased lifetime is resulted from the formation of a special channel of electron transfer. The heterojunctions the triazine-based g-C₃N₄ and heptazine-based g-C₃N₄ phases may well account for the shorter lifetime of PL and higher photocatalytic HER performance.

According to the UV–vis, PL and TR-PL spectra (Fig. 8), the mw-ms-g-C₃N₄ sample is of the highest absorption in the range of UV–460 nm and shows the lowest PL peak emission among the as-obtained g-C₃N₄ samples. Both of the highest absorption and lowest PL emission favor in enhancing its photocatalytic HER performance. According to the results of XPS, EA and XRD, the mw-ms-g-C₃N₄ sample is composed of a hybrid structure of isotype triazine-/heptazine based g-C₃N₄ heterojunctions, which account for the lowest PL emission and less recombination of photo-generated electron–hole pairs. Therefore, the formation of isotype triazine-/heptazine based g-C₃N₄ heterojunction is the key point to improve photocatalytic HER performance.

To determine the bandgap structure of the heptazine-based g-C₃N₄ and triazine-based g-C₃N₄ phases, we calculated the conduction bands (CB) of the er-g-C₃N₄ sample (i.e., heptazine-based g-C₃N₄) and the er-ms-g-C₃N₄ sample (i.e., triazine-based g-C₃N₄), according to the Mott-Schottky equation (Eq. (2)):

$$C_{SC}^{-2} = \frac{2(|E - E_{fb}| - kT/e)}{e\epsilon\epsilon_r N} \quad (2)$$

where e is the electron charge of 1.602×10^{-19} C, ϵ_r is the relative permittivity, ϵ is the vacuum permittivity, N is the carrier density, E is the applied bias at the electrode, and E_{fb} is the flat band potential of a semiconductor (e.g., g-C₃N₄) [29,54]. The Mott-Schottky plots and their corresponding linear fits of the triazine-based g-C₃N₄ (er-ms-g-C₃N₄) and heptazine-based g-C₃N₄ (er-g-C₃N₄) samples are shown in Fig. 9. As Fig. 9a shows, both of the Mott-Schottky plots show positive slopes, suggesting the two samples are n-type semiconductors with electrons as the majority carriers. The flat band potentials (E_{fb}) of the samples can be estimated by extrapolating their linear fits to $1/C^2 = 0$, and give -0.90 V and -0.122 V for the samples of triazine-based g-C₃N₄ (er-ms-g-C₃N₄) and heptazine-based g-C₃N₄ (er-g-C₃N₄), respectively. As Fig. 9b shows, the heptazine-based g-C₃N₄ (er-g-C₃N₄) has a smaller slope than the triazine-based g-C₃N₄ (er-ms-g-C₃N₄), suggesting that the triazine-based g-C₃N₄ sample has a higher carrier density and much faster carrier transfer, agreeing with the photoelectrochemical results (Figs. 2 and 8). According to the Mott-Schottky results

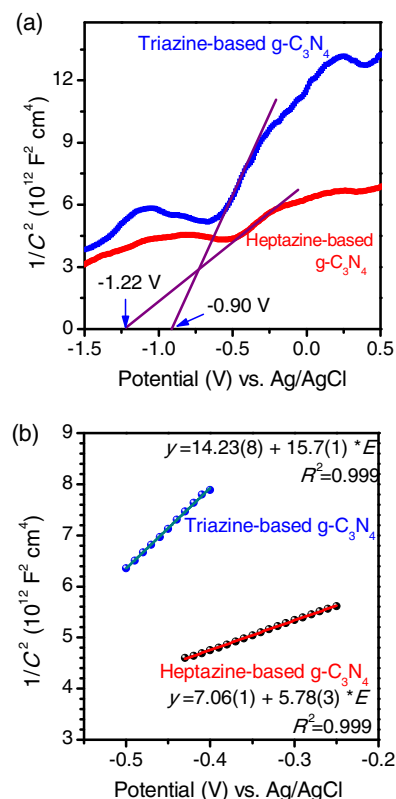


Fig. 9. (a) Mott-Schottky plots of triazine-based g-C₃N₄ (er-ms-g-C₃N₄) and heptazine-based g-C₃N₄ (er-g-C₃N₄); (b) Linear fit plots of the linear parts of Mott-Schottky plots.

(Fig. 9), the conduction bands can be estimated at about -1.22 eV and -0.90 eV for the heptazine-based g-C₃N₄ phase and triazine-based g-C₃N₄ phase, respectively. Combining with their bandgap data ($E_g = 2.66$ eV) determined by their UV–vis spectra (Fig. 8a), one can calculate their valence bands, and the valence bands (i.e., VB) of the heptazine-based g-C₃N₄ and triazine-based g-C₃N₄ samples are 1.44 and 1.76 eV, respectively.

Fig. 10a schematically describes the possible formation mechanism of the isotype triazine-/heptazine based g-C₃N₄ heterojunction during the microwave-assisted molten-salt process using melamine as the single-source precursor. The formation process can be divided into three stages. At the first step (RT–450 °C, 10 °C min^{−1}), some melamine molecules sublime and polymerize to form polymeric melem species. The sublimation point of melamine is ~ 335 °C, and it can form polymeric melem at 389 °C [5]. The melting point of the eutectic KCl/LiCl mixture (49.4:50.6 in molar ratio) is about 450 °C, below which the eutectic mixture is still a solid-state phase. The melamine molecules and the newly-formed melem species are therefore confined in the isolated microcells in the solid KCl/LiCl mixture. At the second step (450–550 °C, 10 °C min^{−1}), the solid KCl/LiCl mixture begins to melt and then provides a special high-temperature liquid media to improve the polymerization reaction of unreacted melamine for the formation of triazine-based fragments. At the third step (550 °C for 30 min), the polymerization reactions of the heptazine-based fragments and triazine-based fragments continue and finally form the isotype triazine-/heptazine based g-C₃N₄ heterojunctions. During the rapid heating of microwave irradiation, some melamine molecules tend to form polymeric melem [53] at the temperature below 450 °C, while the others tend to form the triazine-based g-C₃N₄ species. The newly formed triazine-based g-C₃N₄ and heptazine-based g-C₃N₄ species can be easily connected

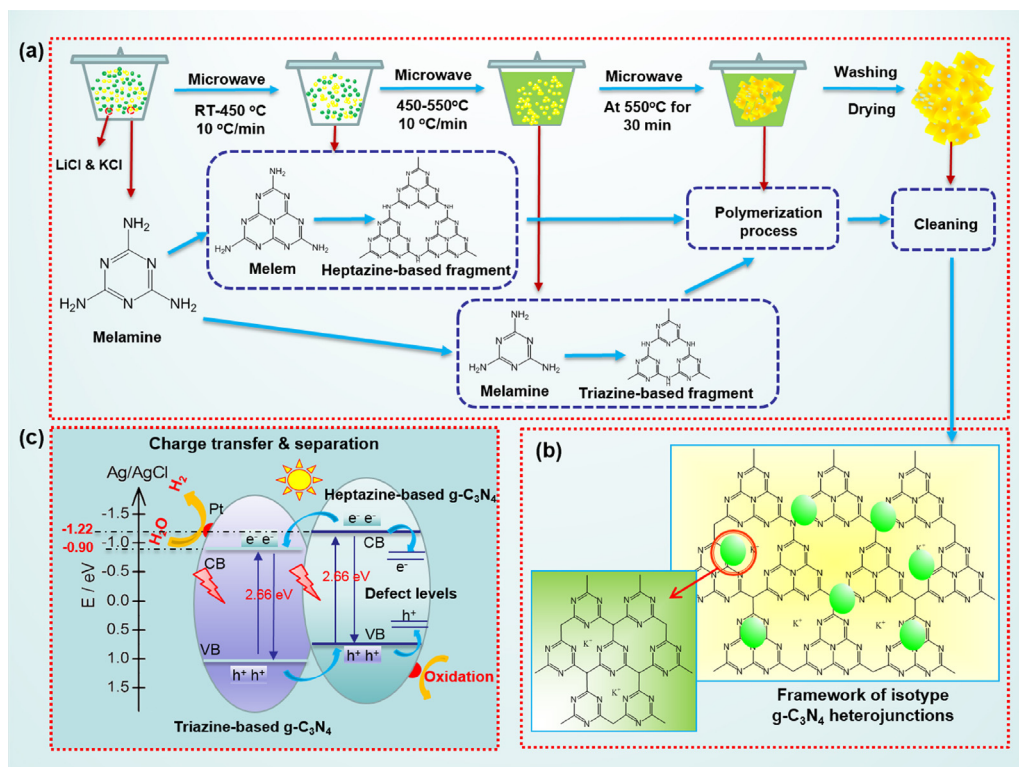


Fig. 10. (a) Possible formation mechanism of isotype triazine-/heptazine based g-C₃N₄ heterojunctions in microwave-assisted molten-salt process; (b) Schematic expression of the isotype g-C₃N₄ heterojunctions; (c) Possible routes for the separation of photogenerated electron-hole pairs and their transfer in the isotype triazine-/heptazine based g-C₃N₄ heterojunctions.

with one another at the molecular level in the confined liquid phase of molten KCl/LiCl (Fig. 10b). For charge balance, some K⁺ ions can be embedded in the voids or spacings of the carbon nitride layers (Fig. 10b). It is worth to note that the molten salt (KCl/LiCl) plays multiple roles: (1) to act as microcells that hinder the agglomeration at the initial polycondensation [12–14]; (2) to offer a special ionic liquid media that favors in the formation of triazine-based units and results in the co-existence of melamine and melem units; (3) to accelerate the absorption of microwave radiation and to achieve a rapid synthesis; (4) to promote the formation of isotype triazine-/heptazine based g-C₃N₄ heterojunctions in a one-pot process using a single-source precursor.

Taking chemical compositions, microstructures and formation process into account, we can conclude the possible reasons why the mw-ms-g-C₃N₄ sample has a higher photocatalytic HER activity than the other g-C₃N₄ samples. First of all, the mw-ms-g-C₃N₄ sample consists of the isotype triazine-/heptazine based g-C₃N₄ heterojunction with a unique electric band structure of type II heterojunction (Fig. 10c), which can provide a more convenient path for the transfer of photo-generated carriers and lead to more efficient separation of photo-generated electron-hole pairs than the other g-C₃N₄ samples obtained [55,56]. Secondly, some defects formed in the mw-ms process, e.g., N vacancies and K⁺ ions adsorbed, can trap carriers to further improve the separation of photo-generated electron-hole pairs. Thirdly, the thin two-dimensional plate-like morphology (Fig. 6) of the heptazine-/triazine-based g-C₃N₄ heterojunctions can shorten the transmission distance and then decrease the recombination probability of the photo-generated electron-hole pairs [15]. Finally, the excellent dispersibility of mw-ms-g-C₃N₄ in water (Fig. S3, ESI†) provides a closer contact with reactants and then enhances its photocatalytic HER performance.

Stability and recycling performance of the mw-ms-g-C₃N₄ sample is shown in Fig. 11a. One can find that the HER performance of the mw-ms-g-C₃N₄ photocatalyst has no obvious deactivation after being illuminated for 12 h under visible light, indicating that the g-C₃N₄ photocatalyst obtained via the microwave-assisted molten-salt process are stable in the present condition. To further corroborate the stability of the mw-ms-g-C₃N₄ photocatalyst, we characterized the re-collected solids after the HER experiment using the XRD technique (Fig. S14, ESI†). One can find that the XRD patterns before and after the photocatalytic HER test are similar, suggesting that there is no obvious change in their phase structure during the HER process.

To check the universality of the photocatalytic effect, we used the g-C₃N₄ samples to photo-degrade organic dyes under visible-light irradiation ($\lambda > 420$ nm). Fig. 11b shows the UV-vis spectra of the RhB aqueous solutions after photodegradation for various times (0–60 min). It is clear that the intensity of the characteristic RhB peak at 551 nm decreases with the increase in the photodegradation time, and the location of the characteristic peak of RhB is not significantly changed. Fig. 11c compares the photodegradation behavior of the g-C₃N₄ samples synthesized by various processes, and Fig. 11d shows their corresponding photodegradation rates (k , min⁻¹). One can find that the sample of mw-ms-g-C₃N₄ is of the highest rate for RhB photodegradation. Therefore the mw-ms-g-C₃N₄ sample is of stable and universal photocatalytic performance, e.g., photocatalytic HER and organic degradation.

To check the generality and practicability of the microwave-assisted molten-salt process in the synthesis of g-C₃N₄ photocatalysts, we designed a series of synthesis using KCl/LiCl mixture with various melting points (353, 400 and 450 °C) at different polymerization temperatures (520, 550 and 580 °C) for various times (15, 30 and 45 min). The XRD, FT-IR, UV-vis DR spectra (Fig. S4 and S6, ESI†) indicate that the samples obtained at 550 °C for

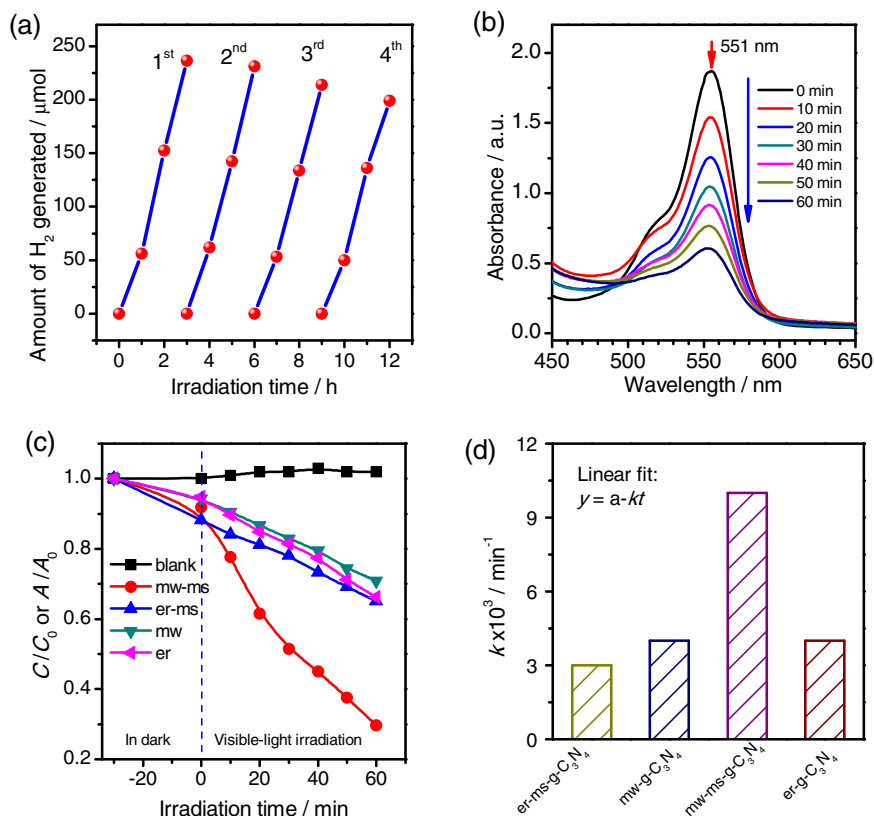


Fig. 11. (a) Stability and recycling hydrogen evolution activity of the g-C₃N₄ sample (mw-ms-g-C₃N₄) obtained via the microwave-assisted molten-salt process; (b) Typical UV-vis spectra of RhB aqueous solutions after photocatalytic degradation for various times using mw-ms-g-C₃N₄ as the photocatalyst (50 mg photocatalyst in 50 mL of 10 mg L⁻¹ RhB solution under visible-light irradiation, $\lambda > 420$ nm); (c–d) Comparison of the photocatalytic RhB degradation activity of the g-C₃N₄ photocatalysts obtained via different processes.

30 min using KCl/LiCl mixtures with various melting points are of a similar phase and chemical composition. The photocatalytic tests (Fig. S7, ESI†) indicate that the samples obtained with the molten salts with higher melting points (400 and 450 °C) have higher HER activities than the sample obtained with lower melting-point molten salt (353 °C). Reaction temperatures in the mw-ms process also have effects on the HER property of g-C₃N₄ samples. The g-C₃N₄ sample obtained at 550 °C has a higher HER activity than the samples obtained at 520 and 580 °C (Fig. S8 and S9, ESI†). In addition, microwave-irradiation time in the mw-ms synthesis has some influence on their photocatalytic HER performance. Under the synthetic conditions with molten salts (m.p. 450 °C) at 550 °C for various times, the g-C₃N₄ sample obtained for 30 min shows a higher HER activity than the samples obtained for 15 min or 45 min (Fig. S10 and S11, ESI†). Therefore, the optimum conditions for the synthesis of g-C₃N₄ samples via the mw-ms process are 550 °C for 30 min using a molten salt of KCl/LiCl with a melting point of 450 °C as the polymerization media. It is worth to note that although the synthetic conditions influence the photocatalytic HER performance, the fluctuation in their HER activity is not so obvious, and the microwave-assisted molten-salt process is therefore a robust approach to synthesize high-performance g-C₃N₄ photocatalysts for HER applications.

To check the effect of heterojunctions between triazine-based g-C₃N₄ and heptazine-based g-C₃N₄ phases on photocatalytic activity, we made a mixture consisting of triazine-based g-C₃N₄/heptazine-based g-C₃N₄ phases by physically mixing the er-g-C₃N₄ and er-ms-g-C₃N₄ (1:1 in mass ratio). The XRD pattern and FT-IT spectra of the mixture are similar to those of the mw-ms-g-C₃N₄ sample (Fig. S13, ESI†). However, the photocatalytic RhB degradation activity (Fig. S12, ESI†) of the mixture is much

lower than that of the mw-ms-g-C₃N₄ sample, suggesting that the heterojunctions between the triazine-based g-C₃N₄ and heptazine-based g-C₃N₄ phases are essentially important in improving their photocatalytic performance.

Table 3 compares the microwave-assisted molten-salt process with some recently reported methods in the synthesis and HER performance of g-C₃N₄ photocatalysts using melamine as the single-source precursor. One can find that the microwave-assisted molten-salt process developed here is of some outstanding advantages: rapid synthesis, high yield, simple process, and high photocatalytic HER performance.

4. Conclusions

The unique isotype heterojunctions of triazine-based g-C₃N₄/heptazine-based g-C₃N₄ have been synthesized by a newly-developed microwave-assisted molten-salt (mw-ms) process using melamine as the single-source precursor for the first time. The mw-ms process combined the advantages of rapid heating of microwave irradiation and high-temperature liquid media of molten salt (KCl/LiCl), which provide a unique condition for the one-pot rapid synthesis of isotype triazine-/heptazine based g-C₃N₄ heterojunctions. The typical isotype g-C₃N₄ heterojunction (55 wt.% in yield) has been synthesized at 550 °C for 30 min, and shows a visible-light driven photocatalytic HER rate of 1480 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is 5 times that (300 $\mu\text{mol g}^{-1} \text{h}^{-1}$) of the er-ms-g-C₃N₄ sample, 15 times that (95 $\mu\text{mol g}^{-1} \text{h}^{-1}$) of the er-g-C₃N₄ sample and 23 times that (63 $\mu\text{mol g}^{-1} \text{h}^{-1}$) of the mw-g-C₃N₄ sample. The typical AQY at 420 nm of the isotype g-C₃N₄ heterojunction is as high as 10.7%. The huge enhancement in HER activity should be attributed to the isotype triazine-/heptazine based g-

Table 3Comparison of the synthesis and HER performance of g-C₃N₄ photocatalysts using melamine as the single-source precursor.

Synthetic process	Yield ^a	Photocatalytic HER performance	Microstructure	Reference
Thermal polymerization with H ₂ SO ₄ pre-treatment (at 600 °C for 4 h in Ar)	<15 wt%	220 μmol g ⁻¹ h ⁻¹ (0.5 wt.% Pt-loading, 10 vol.% TEOA solution, λ > 420 nm)	Bulk	[57]
Thermal polymerization (at 550 °C for 2 h in air)	N/A ^b	355 μmol g ⁻¹ h ⁻¹ (1 wt.% Pt-loading, 80 vol.% methanol solution, λ > 400 nm)	Nanosheets & aggregation	[49]
Molten salt method (at 550 °C for 4 h in air)	N/A	880 μmol g ⁻¹ h ⁻¹ (3 wt.% Pt-loading, 10 vol.% TEOA solution, λ > 420 nm)	Nanosheets & aggregation	[44]
Thermal polymerization (at 400 °C for 1.5 h in air and at 700 °C for 2 h in N ₂)	N/A	3450 μmol g ⁻¹ h ⁻¹ (3 wt.% Pt-loading, 10 vol.% TEOA solution, visible-light)	Nanosheets & aggregation	[58]
Microwave heating (1000 W for 18 min, >1000 °C, closed container)	33%	200 ~ 250 μmol g ⁻¹ h ⁻¹ (0.5 wt.% Pt-loading, 15 vol.% TEOA solution, λ > 420 nm)	N/A	[39]
Thermal polymerization (at 450–520 °C for 2 h; and at 470–540 °C for 2 h in Air)	~40.7%	689 μmol g ⁻¹ h ⁻¹ (3 wt.% Pt-loading, 15 vol.% TEOA solution, λ > 420 nm)	Nanorods & aggregation	[59]
Microwave-assisted molten-salt process (at 550 °C for 15–30 min in air)	54–62%	1480 μmol g ⁻¹ h ⁻¹ (3 wt.% Pt-loading, 10 vol.% TEOA solution, λ > 420 nm)	Nanosheets	this work

^a The mass ratio of obtained solid to its precursor.^b Not available.

C₃N₄ heterojunctions with a suitable configuration in electronic band structures, which provides efficient paths for transport and separation of photo-generated electron-hole pairs. The synergistic effects of microwave heating and molten-salt liquid polycondensation condition provide a robust platform for rapid synthesis of g-C₃N₄ based HER photocatalysts. The mw-ms process is potential method for large-scale synthesis of g-C₃N₄ based HER photocatalysts and other extended material systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.10.014>.

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